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EFFECT OF STRUCTURAL FACTORS ON THE CATALYTIC ACTIVITY OF BETA-DIKETONATES OF 3d-ELEMENTS IN THE THERMAL DECOMPOSITION REACTION OF AMMONIUM PERCHLORATE

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Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ë in Russian, transliterate as yë or ë. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

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RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	$\sin^{-1}$
arc cos	$\cos^{-1}$
arc tg	$\tan^{-1}$
arc ctg	$\cot^{-1}$
arc sec	$\sec^{-1}$
arc cosec	$\csc^{-1}$
arc sh	$\sinh^{-1}$
arc ch	$\cosh^{-1}$
arc th	$\tanh^{-1}$
arc cth	$\coth^{-1}$
arc sch	sech^{-1}
arc csch	csch^{-1}
rot	curl
lg	log

GREEK ALPHABET

Alpha	A	α	∗		Nu	N	ν	
Beta	B	β			Xi	Ξ	ξ	
Gamma	Γ	γ			Omicron	O	o	
Delta	Δ	δ			Pi	Π	π	
Epsilon	E	ε	ϵ		Rho	P	ρ	ϱ
Zeta	Z	ζ			Sigma	Σ	σ	ς
Eta	H	η			Tau	T	τ	
Theta	Θ	θ	ϑ		Upsilon	T	υ	
Iota	I	ι			Phi	Φ	φ	ϕ
Kappa	K	κ	κ	ϰ	Chi	X	χ	
Lambda	Λ	λ			Psi	Ψ	ψ	
Mu	M	μ			Omega	Ω	ω	

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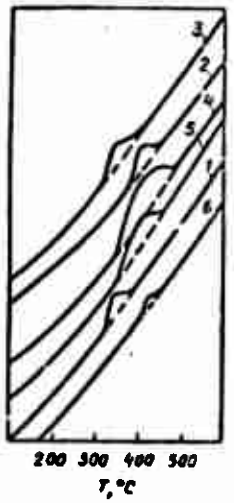
Effect of ~~structure~~ structural factors on the catalytic activity of ~~the~~ β-diketonates of 3d-elements ~~diketonates of electrodialysis elements~~ in the ~~reaction of the~~ thermal decomposition (reaction) of ammonium perchlorate.

In the present work ~~is~~ investigated the effect of the structure factors of the β-dicarbonyl ~~of the~~ compounds of 3d ~~electrodialysis~~

elements on the rate of the nonisothermal decomposition of ammonium perchlorate (PXA). The study of their thermal resistance under conditions of nonisothermal heating in the atmosphere, ~~concentrated by~~ enriched with oxygen, ~~it~~ showed that in the final stage of the decomposition of substance is ~~exhibited~~ manifested the sharp and intense ~~ekzoeffekt~~ exoeffect, which is ~~no in the~~ observed in inert atmosphere or in air [1]. The observed in this case value of heat release distorts the shape of the curve of temperature rise ~~on~~ at 50-60° C (Fig. 1). The presence of this effect and the temperature interval of its manifestation in conjunction with data [2-5] about the effectiveness of tris (~~atsetilatsetonata~~ acetylacetonate) ~~zheleza~~ iron (III) in an increase in the rate of combustion of some systems ~~on the basis of~~ with a base PXA and nitromethane give grounds to assume that the investigated compounds will turn out to be catalytically active in the processes of the thermal decomposition of PXA and similar oxidizers.

**********EDITOR: PLEASE CHECK FOR ALL CYRILLIC OR UNCLEAR ITEMS ON THE TABLE (FIGURE) WHICH MAY HAVE BEEN LEFT OUT**********

Fig. 1. Nature of the distortion of the shape of the curve of temperature rise during formation of thermographs of acetylac ~~at the tetradgra:irrvanii of ats:cilatsctonatov~~ in the atmosphere, enriched ~~concentrated~~ by oxygen (according to data in [1]): 1 - [Cu $(C_5H_7O_2)_2$]; 2 - [CO $(C_5H_7O_2)_2$]; 3 - [CO $(C_5H_7O_2)_3$]; 4 - [Mn $(C_5H_7O_2)_3$]; 5 - [Fe $(C_5H_7O_2)_3$]; 6 - [CR $(C_5H_7O_2)_3$].



In our investigations ~~utilizal~~ we used a specimen/sample of the PXA of industrial ~~izgotavlenija~~ manufacture with average particle size ~30 μ.

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The conditions of the obtaining and property of the investigated by us β-~~dikarbonilnyx~~ dicarbonyl compounds Mn^{3+}, Mn^{2+}, Cu^{2+}, Co^{3+}, Co^{2+}, Fe^{3+}, Cr^{3+} on the basis of acetylacetone, benzoyl acetone, ~~dibenzoilmetana~~ dibenzoylmethane, ~~tenoiltrifторatsetona~~ tenoyltrifluoroacetone, benzoyltrifluoroacetone and 3-nitroacetylacetone are described earlier [6, 7].

~~For the safeguard for even~~ To ensure uniform distribution of catalyst in the bulk of the specimen/sample of PXA is used the procedure, described in work [1]. The effect of the indicated compounds on rate and nature of the decomposition of PXA was investigated by thermogravimetric method on derivatograph [8], equipped with the system of the ~~suction~~ extraction of decay products from the heated space, which largely eliminated the possible

effect of gaseous decay products on the kinetics of decomposition.

(weighed quantity) ~~sample~~ - 50 mg, the average rate of climb of temperature is 19° C ~~in~~ per min, on straight portion - 22° C ~~in~~ per min, the content of catalyst is 1o/o of the weight of PXA).

Table 1.

**********EDITOR: PLEASE CHECK FOR ALL CYRILLIC OR UNCLEAR ITEMS ON THE TABLE (FIGURE) WHICH MAY HAVE BEEN LEFT OUT**********

Table 1. Effect of the β-~~ditartonatov~~ diketonates of d-elements of the type [M^{n+} $(RCOCHCOR)_n$] ~ ~~to~~ on rate and nature of the thermal decomposition of PXA.

Key: (1) catalyst; (2) temperature (°C) and the ~~loss/depreciation~~ reduction in of the mass (o/o) of the first and second ~~ekzoeffektov~~ exoeffects; (3) the temperatures of beginning and end of the ~~loss/depreciation~~ reduction in of mass; (4) ~~charge~~ t_{decomp} 80% of the weighed quantity of ПХА, ~~;~~ (5) ligand.

Table 1. Effect of the β-diketonates of d-elements of the type $[M^{n+}(RCOCHCOR)_n]$ on rate and nature of the thermal decomposition of PXA.

(1) Катализатор		(2) Температура (°С) и убыль массы (%) первого и второго экзоэффектов				(3) Температуры начала и конца убыли массы			(4) $t_{разл}$ 80% навески ПХА, мин
M^{n+}	(5) лиганд	T_1	Δm_1	T_2	Δm_2	$\vartheta_н$	$\vartheta_к$	$\Delta\vartheta$	
—	—	325	15	460	85	300	455	155	7,0
Co^{2+}	$CH_3COCHCOCH_3$	315	100	—	—	297	318	21	1,0
Co^{3+}		320	83	360	17	290	320	30	1,4
Mn^{2+}		295	24	335	76	300	335	35	1,6
Cu^{2+}		320	85	375	15	280	322	42	1,9
Fe^{3+}		335	16	400	84	300	390	90	4,1
Cr^{3+}		325	15	460	85	300	460	160	7,3
Co^{3+}	$CH_3COCHCOC_6H_5$	310	—	378	100	320	372	52	2,4
Mn^{3+}		335	100	—	—	315	355	40	1,8
Cu^{2+}		315	85	370	15	302	328	26	1,2
Fe^{3+}		340	15	425	85	326	430	101	4,7
Cr^{3+}		329	15	400	85	298	420	122	5,5
Co^{3+}	$C_6H_5COCHCOC_6H_5$	335	81	410	19	325	350	25	1,1
Mn^{3+}		334	53	388	47	320	380	60	2,7
Cu^{2+}		320	85	372	15	313	329	16	0,7
Fe^{3+}		335	15	408	85	322	410	88	4,0
Cr^{3+}		310	15	440	85	318	450	132	6,0
Cu^{2+}	$CF_3COCHCOC_6H_5$	315	80	355	20	295	325	30	1,4
Mn^{2+}		315	15	360	85	300	372	72	3,3
Cu^{2+}	$CF_3COCHCOC_4H_3S$	320	91	360	9	310	330	20	1,0
Mn^{2+}		322	15	365	85	310	370	60	2,7
Co^{3+}	$CH_3COC(NO_2)COCH_3$	360	100	—	—				0,7
Cu^{2+}		320	75	370	25				
Cr^{3+}		310	15	400	85				

The data on effect β-diketonates on the rate of nonisothermal decomposition of PXA are represented in Table 1.

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All the investigated compounds, with the exception of the tris (acetylacetonate) of chromium (III), are catalytically active in the process of the thermal decomposition of PXA under nonisothermal conditions and accelerate this process to 10 times. Most effective from the viewpoint of shortening the duration of process as a whole turn out to be the compounds, which affect predominantly the initial stages of the decomposition of PXA (Fig. 2). The most effective of the number of examined compounds increase the degree of the conversion of PXA from 15 to 75 - 100%. It is characteristic that the temperature of the manifestation of the first exothermic effect on the decomposition curve of PXA does not undergo substantial changes; however, the

temperature interval of the full ~~expansion~~ decomposition of PXA in the presence of catalysts sharply is reduced in accordance with the degree of s' ortening in the duration of the process of decomposition of the ~~charge~~ weighed quantity of PXA. The most effective catalysts prove to be ~~the~~ derivatives Cu^{2+} and CO^{2+}, are least are active - Fe^{3+} and Cr^{3+}. Intermediate position ~~they~~ are occupy ~~β-diketonaty~~ β-diketonates Co^{3+}, Mn^{3+} and Mn^{2+}.

In proportion to the complication of organic ligand is ~~raised~~ increased catalytic activity in accordance with a change in the electron-donor properties of ligands. This fact finds natural explanation under the assumption about the initiation of the ~~considered~~ examined reaction by means of the transfer (redistribution) of charge ~~with~~ during the coordination of reagents with catalyst, since in this case, according to [9], catalytic activity depends on the donor-acceptor properties of partners, which are determined by the Fermi level and by the oxidation-reduction (catalytic) capacities of reagents and catalyst. The latter completely ~~determined form~~ definitely depend on the parameters of the electronic structure of molecules. Actually (Table 2), there is a determined interrelation between the stability of the β-diketonate

about which we ~~is~~ judge from the value of force constant connection M - O [10], and the value of the catalytic activity, which ~~grow/rises~~ increases in proportion to an increase in the stability of catalyst. The indirect confirmation of this conclusion ~~derivation~~ are the data in Tables 1 on ~~larger~~ greater, ~~the acetylacetonatami of the~~ acetylacentonates, in comparison with catalytic activity of ~~khelator~~ chelates on the basis of the more complex ligands, which are characterized, as this is shown in [1, 7], by larger ~~its own~~ natural thermal resistance.

**********EDITOR: PLEASE CHECK FOR ALL CYRILLIC OR UNCLEAR ITEMS ON THE TABLE (FIGURE) WHICH MAY HAVE BEEN LEFT OUT**********

Table 2. Dependence of the catalytic activity of the β-diketonates of d-elements of the type $[M^{n+}(RCOCHCOR^1)_n]$ in the process of the thermal decomposition of PXA on the parameters of the structure of catalyst.

Key: (1) β-diketonate; (2) σ* in β-diketones; (3) t_{decomp} 80% of the weighed quantity of ПХ (4) M-O, $K \cdot 10^{-5}$, dyne/cm [10]

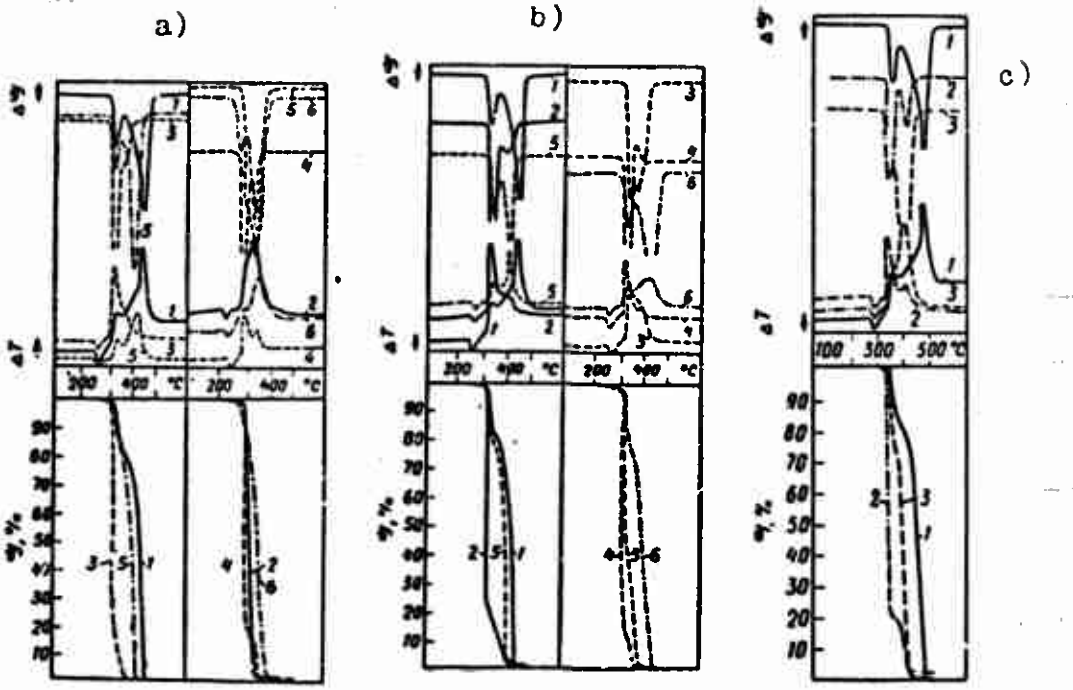
Table 2. Dependence of the catalytic activity of the β-diketonates of d-elements of the type $[M^{n+}(RCOCHCOR^1)_n]$ in the process of the thermal decomposition of PXA on the parameters of the structure of catalyst.

(1) β-Дикетонат	(4) M···O, $K \cdot 10^{-5}$, дин/см [10]	(2) σ* в β-дикетонах [11—12]	$t_{разл}$ 80% (3) навески ПХА, мин
$[Fe(C_5H_7O_2)_3]$	1,65	0	4,1
$(Cu(C_5H_7O_2)_2)$	2,20	0	1,9
$[Co(C_5H_7O_2)_3]$	2,40	0	1,4
$[Cu(C_{10}H_9O_2)_2]$	—	0,6	1,2
$[Cu(C_{16}H_{11}O_2)_2]$	—	1,2	0,7
$[Cu(C_6H_4O_2SF_3)_2]$	—	3,0	1,0
$[Cu(C_{10}H_6O_2F_3)_2]$	—	3,2	1,4
$[Cu[(CH_3CO)_2CNO_2]_2]$	—	3,5	0,7

**********EDITOR: PLEASE CHECK FOR ALL CYRILLIC OR UNCLEAR ITEMS ON THE TABLE (FIGURE) WHICH MAY HAVE BEEN LEFT OUT**********

Fig. 2. Derivatogram of PXA with addition of 1% of β-diketonates (average rate of rise of the temperature 19° C per min).

a) the benzoylacetonates: (1 - PXA; 2 - PXA + [CO $(C_{10}H_9O_2)_3$]; 3 - PXA + [Mn $(C_{10}H_9O_2)_3$]; 4 - PXA + [Cu $(C_{10}H_9O_2)_2$]; 5 - PXA + [Fe $(C_{10}H_9O_2)_3$]; 6 - PXA + [CR $(C_{10}H_9O_2)_3$]. b) the dibenzoylmethan: 1 - PXA; 2 - PXA + [CO $(C_{15}H_{11}O_2)_3$]; 3 - PXA + [Mn $(C_{15}H_{11}O_2)_3$]; 4 - PXA + [Cu $(C_{15}H_{11}O_2)_2$]; 5 - PXA + [Fe $(C_{15}H_{11}O_2)_3$]; 6 - PXA + [CR $(C_{15}A_{11}O_2)_3$]. c) the benzoyltrifluoroacetonates: 1 - PXA; 2 - PXA + [Cu $(C_{10}H_6O_2F_3)_2$]; 3 - PXA + [Mn $(C_{10}H_6O_2F_3)_2$].



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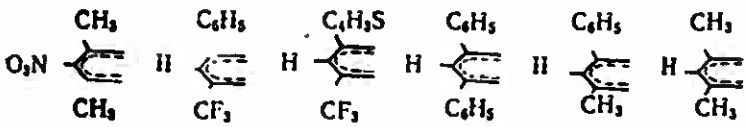
The experimental data make it possible to arrange the investigated β-diketonaty according to the degree of the effect of substituent's nature on catalytic activity in the following series:



The obtained sequence indicates ~~testifies to~~ the presence of the correlation between the catalytic activity of β-diketonatoy in the reaction of the thermal decomposition of PXA and the total ~~inductive~~ induction constant σ * of taffeta ~~the taffeta of the~~ substituents [11, 12] in β-diketone (Table 2), which is the ~~by the being~~ indirect characteristic of the degree of localization of electron density (value of effective charge) on the central ion of metal. The observed in this case certain

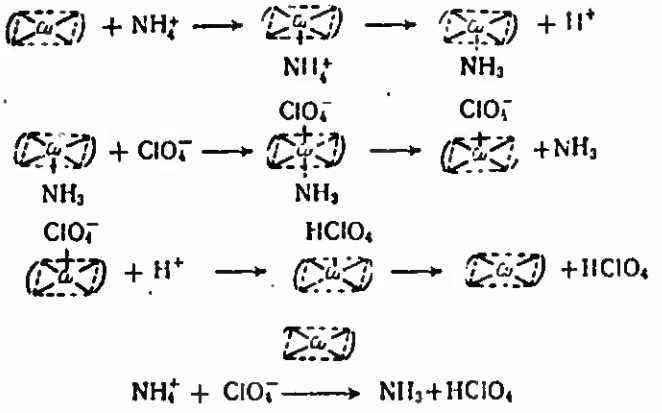
disturbance/breakdown of law (of the change) in the lower part of the Table, apparently, is connected with ~~distinctions~~ differences in the effect of the investigated compounds on the final stages of the decomposition of PXA (Fig. 2).

Difficulties in the study of process are here connected also with the large curvature of the corresponding sections of the curves of DTG [ДТГ - derivatograms].

The obtained results give grounds to assume ~~to be~~ participation in the ~~event/report~~ event of catalysis of the d-electron of metal and to determine the direction of the transfer of charge in system (of) catalysts-reagents. From them also it follows that in spite of the widespread opinion, in accordance with which the catalysts of the thermal decomposition of PXA take part predominantly in the high-temperature reactions of heterogeneous decomposition of ~~khloroy~~ perchloric acid and oxidation of ammonia [13], at least, under some conditions, catalyst contributes also to acceleration and the low-temperature stage of the decomposition of PXA, which leads to formation (of) $HClO_4$ and NH_3.

The findings make it possible to assume the following diagram of

the mechanism of this process (in an example of the ~~chelatov~~ Chelates of copper (II)):



$$NH_4^+ + ClO_4^- \longrightarrow NH_3 + HClO_4$$

The proposed mechanism agrees with known charge distribution on the atoms bis-(~~acetylacetonate~~ acetylacetonate) of copper (II) [14]. The velocity of the coordination of ammonium ion and the ~~cleavage~~ splitting of proton (especially the ~~cleavage~~ splitting of proton) ~~it~~ depends on the value of positive charge on the atom of transition metal. It must be noted also that this complex can coordinate the determined atomic groupings on ~~shch~~ the 5th or 6th place.

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This mechanism agrees also with the established above dependence of catalytic activity on the value of effective charge on central atom.

This diagram of the mechanism of catalytic decomposition PXA agrees well with the conventional concepts about the mechanism of the ~~nekitaliticheskogo~~ noncatalytic decomposition of PXA. The examined diagram can be, apparently, transferred, also, to octahedral complexes, if one considers that during the first stage of reaction under the considered conditions can occur the temperature ~~clearage~~ splitting of ligands and they become coordinat~~i~~on-~~n~~ non-saturated, in the same way as this was observed in work [15] during the study of the thermal resistance of the coordinat~~i~~on-saturated complexes on the basis of the β-diketonat~~e~~es of cobalt (II). It goes without saying that the possibility of the realization of concrete intermediate stages requires supplementary substantiation and experimental confirmation. Nevertheless it seems that the findings can be the basis of the directed search for the catalysts of the ~~considered~~ examined process. Preferable turn out to be complexes with the low value of effective charge on the atom of metal and, therefore, with ligands with the large positive values of the inductive constants of the substituents.

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